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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 27, 1993		3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Synthesis and Structure of a Seven Membered Cyclic Cumulene				5. FUNDING NUMBERS G-N00014-91-J-1043	
6. AUTHOR(S) Donald P. Hsu, William M. Davis and Stephen L. Buchwald					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Massachusetts Institute of Technology 77 Massachusetts Avenue Cambridge, MA 02139				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Department of the Navy Arlington, VA 22217-5000				10. SPONSORING/MONITORING AGENCY REPORT NUMBER Technical Report No. 4	
11. SUPPLEMENTARY NOTES Prepared for publication in the <i>Journal of the American Chemical Society</i>					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release and sale, distribution unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This paper describes the preparation and structural characterization of a distorted seven-membered cyclic cumulene. This complex was formed unexpectedly by the reaction of 1,4-bis(trimethylsilyl)buta-1,3-diyne and the <i>in situ</i> prepared zirconocene complex of <i>n</i> -butene.					
93-12384 					
14. SUBJECT TERMS metallacycle, strained organic molecule, cumulene				15. NUMBER OF PAGES 6	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL		

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1043

R & T code 4135014

Technical Report No. 4

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Prepared for Publication

in the

Journal of the American Chemical Society

Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139

May 27, 1993

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The Synthesis and Structure of a Seven Membered Cyclic Cumulene

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Abstract

The reaction of 1,4-bis(trimethylsilyl)buta-1,3-diyne with the *in situ* prepared zirconocene complex of *n*-butene, unexpectedly, produces a distorted seven-membered cyclic cumulene. This novel complex has been characterized spectroscopically and by X-ray crystallography.

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Johnson and coworkers have reported the smallest isolated cyclic cumulene (cyclonona-1,2,3-triene)^{2a} and the smallest example to be generated and trapped *in situ* (cyclohexa-1,2,3-triene).^{2b} Herein we report the synthesis and X-ray crystal structure determination of a seven-membered cyclic cumulene, 2,4,7-tris(trimethylsilyl)-3-trimethylsilyl-ethynylzirconacyclophepta-2,4,5,6-tetraene.³

In an attempt to prepare zirconaradialene **1**, 1,4-bis(trimethylsilyl)buta-1,3-diyne **2** was treated with *in situ* prepared zirconocene complex of *n*-butene **3**,⁴ at -78° C, followed by warming the reaction mixture to room temperature which led to the isolation of two compounds, **4** (1:2 adduct of Cp₂Zr and **2**) and **5** (2:1 adduct of Cp₂Zr and **2**).⁵ The yield of **4** was optimized by performing the reaction using a 1:2.5 ratio of the zirconocene reagent and **2**. Under these conditions **4** was isolated in 66% yield after recrystallization from diethyl ether at low temperature.

Description of **4** as a distorted cumulene, rather than as the isomeric zirconacyclopentadiene **6**, follows from its X-ray crystal structure; the ORTEP

Scheme 1

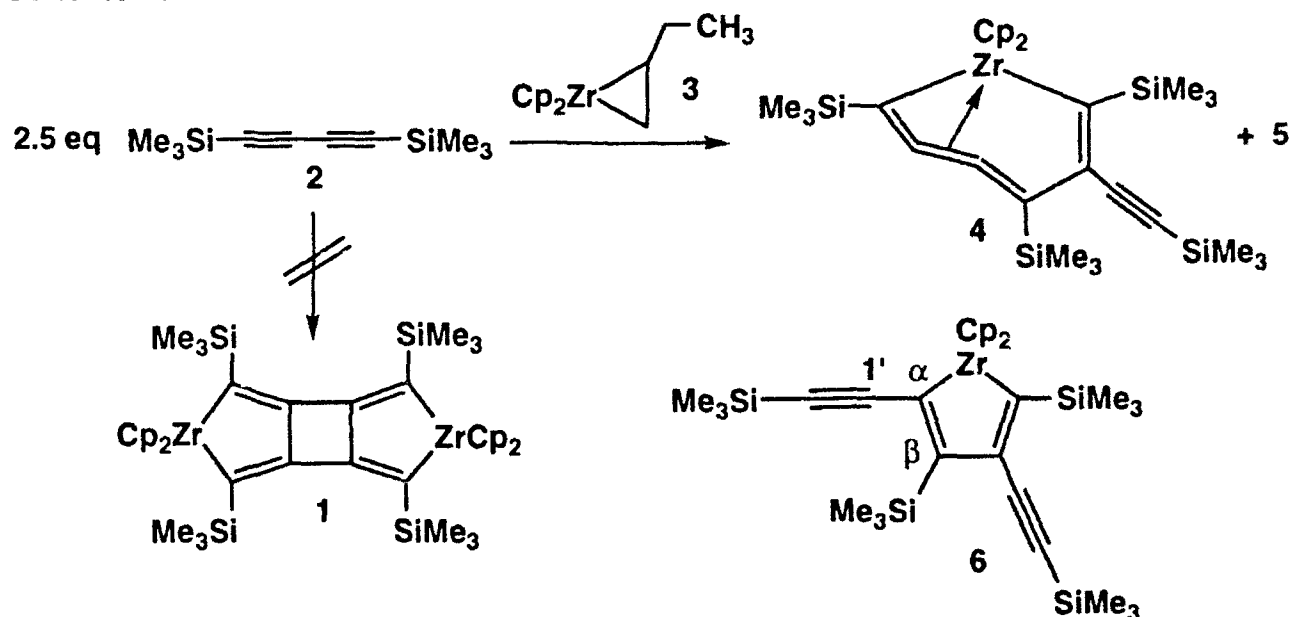
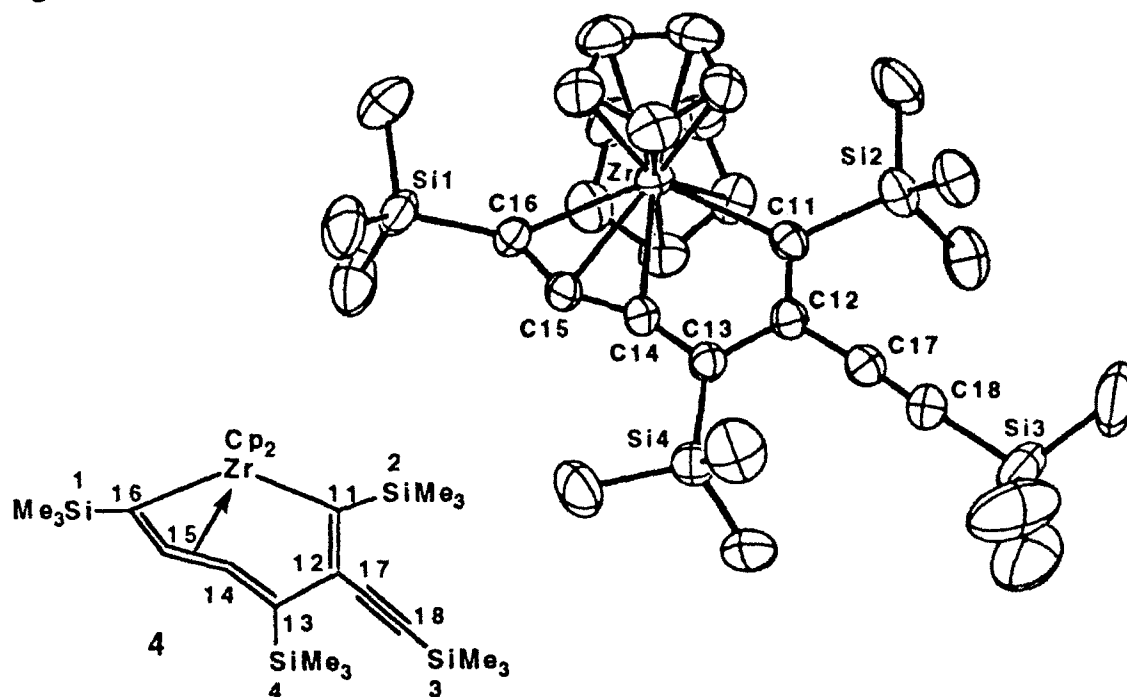


diagram and selected bond lengths and angles for **4** are shown in Figure 1. For example, the bond lengths for C13-C14 [1.337(6)], C14-C15 [1.298(6)] and C15-C16 [1.279(6)] indicate that these are of roughly similar bond order. Certainly the C14-C15 distance is incompatible with its description as a C-C single bond.^{3a} The bond angles for **4** are also consistent with its formulation as a cumulene, but

indicate a great deal of distortion from linearity, as would be expected in order to minimize ring strain. For example, the C13-C14-C15 angle [160.1(5)°] is

Figure 1



Selected Bond Lengths and Angles for 4: Lengths (Å) Zr-C11 2.416(5), Zr-C14 2.396(5), Zr-C15, 2.423(5), Zr-C16 2.442(5), C13-C14, 1.337(6), C14-C15, 1.298(6), C15-C16, 1.279(6), C17-C18, 1.205(7), C12-C17, 1.452(7). Angles (°) C11-C12-C17, 124.9(5), C13-C14-C15, 160.1(5), Si1-C16-C15, 143.6(4), Si3-C18-C17, 176.3(6), C14-C15-C16, 148.8(5), C12-C17-C18, 177.9(6), C11-Zr-C16, 128.6(2), C15-Zr-C16, 30.5(2).

significantly perturbed from the idealized value of 180°.⁶ Moreover, the C14-C15-C16 angle [148.8(5)°] reflects an even more drastic deviation and is midway between that expected for sp and sp² hybridization at C15. These angles are similar to the value of 155.4(3) reported by Wojicki and coworkers for the related d⁰ allene complex, Cp₂Zr(CH₃)(η³-C(Ph)=C=CH₂).^{3a} In contrast, the Cβ-Cα-C1' angle for structure 6 would be expected to be ~125° in comparison with two relevant structurally characterized zirconacyclopentadienes.⁷ A further interesting structural feature is that the metallacyclic portion of 4 is essentially planar.⁸

To date, we have not examined the reaction chemistry of 4 in detail, but we have shown that it survives, largely unchanged, heating as a benzene solution at 75° C for three days. If the thermolysis is carried out in the presence of excess

PMe₃, no conversion to a characterizable product is seen; only slow decomposition of **4** is observed.

While the route by which **4** is formed is unclear, it is reasonable to invoke the intermediacy of **6**. Severe in-plane steric interactions between the ring substituents⁹ could induce the zirconocene unit to migrate from C14 to C16.^{3a} Several reasons for the relative stability of **4** are likely. First, coordination of the central double bond of the cumulene produces a coordinately saturated zirconium center. Such intramolecular coordination of olefins in related systems is well precedented.¹⁰ The π -system of the central double bond is in the metallacyclic plane, facilitating its interaction with the Zr-centered LUMO.¹¹ We note that **4** is different than the many zirconocene complexes of strained unsaturated organic molecules which we have reported.^{9b} In these molecules, the strain is attenuated by backbonding from a d² zirconium center; such a means of stabilization is obviously not available for this d⁰ complex. Second, Zr-C bond lengths (Figure 1) are significantly longer than C-C bond lengths, which mitigates the ring strain.^{2c,3c} In addition, Zr-C bonds in which the carbon center has a trimethylsilyl substituent possess increased stability.^{9a} Finally, the thermal stability of **4** is not entirely surprising; the bulky trimethylsilyl substituents at C13 and C16, as well as the enormous zirconocene unit, sterically protect the cumulene moiety. This minimizes the likelihood of bimolecular reactions of **4**,^{2c} whether they be dimerization or nucleophilic attack.

In summary, we have prepared the smallest ring cyclic cumulene to be structurally characterized.¹² The results reported herein indicate that the combination of transition metals and serendipity can lead to unexpected and interesting new chemistry.

Acknowledgment. This research was supported, in part, by the Office of Naval Research, to whom we are grateful. SLB acknowledges additional support as a Fellow of the Alfred P. Sloan Foundation and as a Camille & Henry Dreyfus Teacher-Scholar. We thank Dr. Richard D. Broene and Mr. Benjamin P. Warner for helpful discussions and Mr. Scott C. Berk for calculating the bond angles of the zirconacyclopentadienes from reference 7.

Supplementary Material Available: Crystallographic data and procedures, ORTEP and PLUTO diagrams of **4**, tables of bond distances and angles for **4**, and a

table of final positional and thermal parameters for **4**; table of structural factors for **4** (80 pages). Ordering information is given on any current masthead page.

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12. Experimental procedure for the preparation of **4**: To a solution of zirconocene dichloride (0.292 g, 1 mmol) in ether (20 mL) at -78 °C, under an argon atmosphere, was added a solution of *n*-butyllithium (1.14 M in hexane, 1.75 mL, 2 mmol) dropwise. After 30 min, a solution of 1,4-bis(trimethylsilyl)-1,3-butadiyne (0.488 g, 2.5 mmol) in ether (10 mL) was added, the cold bath was removed and the reaction was allowed to stir overnight at room temperature. At this point, the solution was cannula-filtered, and the volatiles were removed *in vacuo* to give a crude product which was recrystallized from diethyl ether at -80 °C to yield **4** as a yellow solid (0.401 g, 66%): ¹H NMR (300 MHz, C₆D₆) δ 5.38 (s, 10 H), 0.66 (s, 9 H), 0.58 (s, 9 H), 0.35 (s, 9 H) and 0.31 (s, 9 H); ¹³C NMR (75 MHz, C₆D₆) δ 229.2, 187.8, 162.7, 161.4, 152.3, 110.0, 105.3, 101.0, 91.6, 3.3, 1.3, -0.1 and -0.2; IR (KBr) 2955, 2894, 2123, 1875, 1649, 1441, 1438, 1397, 1265, 1250, 1244, 1080, 1018, 989, 840, 812, 805, 799, 794, 755, 693, 679, 669, 634, 628, 484, 437 and 431 cm⁻¹; Anal. Calcd. for C₃₀H₄₆Si₄Zr: C, 59.05; H, 7.6. Found: C, 58.94; H, 7.44.

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